Mathematical Modeling and Analysis

Effect of Electrostatic Interaction on Deposition of Colloid on Partially Covered Surfaces

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The adsorption and deposition (irreversible adsorption) of colloids and bioparticles at solid/liquid interfaces are of great significance in many natural and practical processes such as water and wastewater filtration, membrane filtration, papermaking, flotation, protein and cell separation, enzyme immobilization, membrane biofouling, and artificial organ transplant. Often in these processes, especially in filtration, polydisperse suspensions or mixtures appear, e.g., colloid/polymer, colloid/macroscopic particle, or protein/surfactant. As a result of their higher diffusivity, the smaller components of the mixture will adsorb preferentially at the interface, forming a layer that may prohibit consecutive deposition of larger particles. This effect leads to a considerable decrease in the kinetics of larger-particle accumulation at the interface. Similar problems often appear in model experiments concerned with protein or colloid-particle adsorption when the usual substrate cleaning procedure may produce a nanosized contaminant layer difficult to detect by conventional means. In respect to both charge distribution and geometry, formation of such a layer will produce surface heterogeneity, which is expected to influence the kinetics and maximum coverage of the adsorption experiments. Thus, modeling of adsorption phenomena at precovered surfaces seems an important and challenging task that can be accomplished using a variety of approaches. Among them, the random sequential adsorption (RSA) approach seems to be the most suitable one because of its simplicity and efficiency.

The classical RSA model considers a sequence of trials of particle adsorption on a homogeneous interface. Once an empty surface element is found, the particle is permanently fixed, with no consecutive motion allowed. Otherwise, the virtual particle is rejected and a next-addition attempt is undertaken. Since the 1980s a number of extended RSA models have been developed that include the effects of particle shape, Brownian motion, external force, particle-particle and particle-interface electrostatic interaction, colloid-particle polydispersity, and surface heterogeneity. The results based on RSA simulations allow us to predict particle monolayer structure and the jamming coverage of particles. One may use the model to predict particle-adsorption kinetics as well, although depending on the particle-transport mechanism, an appropriate analysis of real adsorption problems can require inclusion of a correction for bulk transport or the hydrodynamic scattering effect. Thus, RSA modeling can be a powerful tool in the study of irreversible adsorption of macromolecules, proteins, and colloid particles.

As discussed in Ref. [1], however, both existing 2D and 3D RSA models that consider the effects of electrostatic interaction, often exploited for the interpretation of experimental results, are greatly simplified, and their application to colloidal systems can result in incorrect predictions. Specifically, neglecting the particle-surface interaction at a distance from the adsorption surface in the 2D model can result in overestimating the surface blocking effect, while the assumption of the rectilinear particle trajectory in the model 3D can lead to inaccurate pair correlation functions. Therefore, the goal of this research is to develop a new, more realistic adsorption approach. In the new model, the adsorbing particle curvilinear trajectory is calculated according to the forces acting on the particle, starting from the point where the energy barrier was found up to the point corresponding to the particle-interface contact. This modification delivers a new model that we call curvilinear trajectory (CT) RSA.

Using this model we can calculate the available surface function or the particle adsorption probability B_l as a function of the small and large particle surface coverage $\theta_i = \pi a_i^2 N_i$, where a_i and N_i are the radius and surface density of the particle i; $i = s, l$; and the subscripts s and l refer to small and large particles, respectively [2]. The results obtained for the particles' size $a_l = 500$nm; $a_s = 250$nm; parameter $\kappa a_l = 8$, where κ^{-1} is the Debye screen length; and two values of the small particle surface coverage: $\theta_s = 0$ (reference curve) and $\theta_s = 0.08$ are presented in Fig. 1. This figure presents the results obtained with the models 2D and 3D RSA as well.

Comparison of the available surface functions presented if Fig. 1 suggests that both 3D and CT models give identical results at $\theta_s = 0$ and low surface coverage of the large particle, which results from the similar construction of the algorithms. A small difference suggesting different monolayer structures becomes visible at $\theta_l = 0.15$. The difference grows with an increase of the surface coverage, so one could expect somewhat different

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jamming limits. As one can see, the available surface functions are always larger than their 2D counterparts, although the differences are very small at low surface coverage. This difference results from the fact that, unlike the 2D model, the 3D and CT models estimate the adsorption probability by taking into account the value of the particle potential calculated at some distance from the interface and therefore at larger particle-particle distance. Moreover, the interparticle repulsion is partially neutralized because of the attraction to the interface. The 2D model neglects the 3D effects. Therefore, it seems that application of the 2D model is limited to the monodisperse systems and low-to-medium surface coverage or high ionic strength ($\kappa a_l > 100$). On the contrary, the 3D model seems suitable for computing the kinetic aspects of adsorption in the full range of the κa_i parameters.
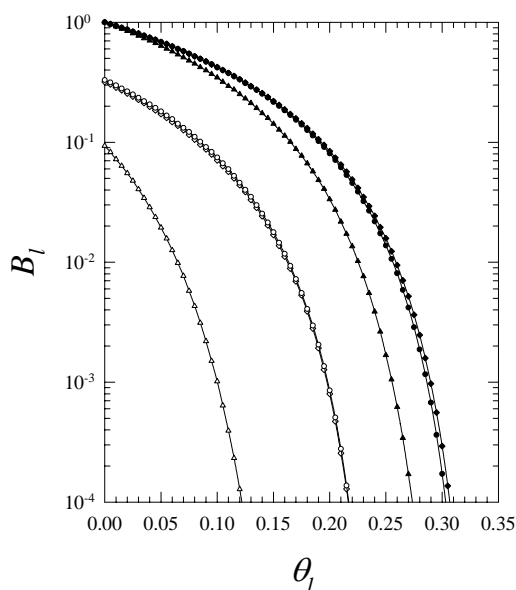

Fig.1. Comparison of the available surface functions $B_l(\theta_l)$ computed with three RSA models for the particle size ratio $a_l/a_s=2$, parameter $\kappa a_l=8$, where κ^{-1} is the Debye screen length, and two values of the small particle surface coverage: $\theta_s=0$ (filled symbols, reference curve) and $\theta_s=0.08$ (open symbols). Triangles, diamonds, and circles correspond to 2D, 3D, and CT model predicted results, respectively.

Fig. 2 presents a comparison of the pair-correlation functions $g_l(R)$ of the monodisperse system computed with the 2D, 3D, and CT models for the following parameters: $a_l=500nm$, $\kappa a_l=10$, and $\theta_l=0.25$ [2]. The high maximum evident in the figure, obtained with the CT model, results from including the rolling effect in the model. In agreement with the algorithm and the available surface functions presented in Ref. [2], the correlation function computed with the 3D model is shifted toward the smaller interparticle distance, corresponding to the stronger lateral repulsion. At the particle-particle distance larger than three particle radii, both 3D and CT models give very similar results. All the three functions are basically indistinguishable at the distance larger than four radii a_l.
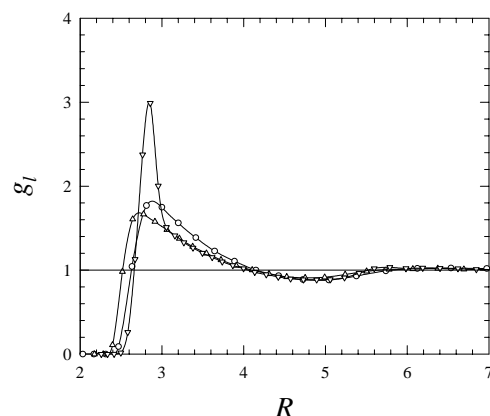

Fig.2. Comparison of radial distribution functions $g_l(R)$ based on simulation data obtained with three RSA models: 2D (circles), 3D (triangles up), and CT (triangles down). The results refer to the monodisperse system ($\theta_s=0$) at the parameter $\kappa a_l=10$ and the large-particle surface coverage $\theta_l=0.25$, $R=r/a_l$.

Acknowledgements

References

[1] P. Weronski, Effect of Electrostatic Interaction on Deposition of Colloid on Partially Covered Surfaces. I. Model Formulation. *Colloids Surfaces A*, accepted.

[2] P. Weronski, Effect of Electrostatic Interaction on Deposition of Colloid on Partially Covered Surfaces. II. Results of Computer Simulations. *Colloids Surfaces A*, accepted.